Structural relaxation and oxygen vacancies in Ca and Y co-doped bismuth iron garnet thin films

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Pulsed Laser Deposition (PLD) growth of ternary system containing Bi and Fe can be challenging due to Bi high volatility. For example, the formation of secondary iron oxide phase has been reported for $BiFeO_3$ [1]. Bismuth iron garnet (BIG, $Bi_3^{3+}Fe_5^{3+}O_{12}^{2-}$) is an insulating [2,3] ferrimagnet oxide with remarkable magneto optical properties [4] that can solely be grown as nanostructures. While pure Single-phase BIG thin films were already achieved and well characterized regarding their structural and chemical properties [5], here, we synthesised crystalline thin film of Ca and Y co-doped bismuth iron garnet (CaY:BIG, $Bi_{2.5}^{3+}Ca_x^{2+}Y_{0.5-x}^{3+}Fe_5\,O_{12-\delta}^{2-}$) also by PLD on gadolinium gallium garnet (GGG) in order to create room temperature magnetic semiconductors. The Bi/Y ratio is modulated to control the magneto optical properties. Improved electrical conductivity values, i. e. more than 7 orders of magnitude higher than pure yttrium iron garnet were obtained and further high/low resistivity states were achieved via post-annealing treatment for the first time in this BIG structure.

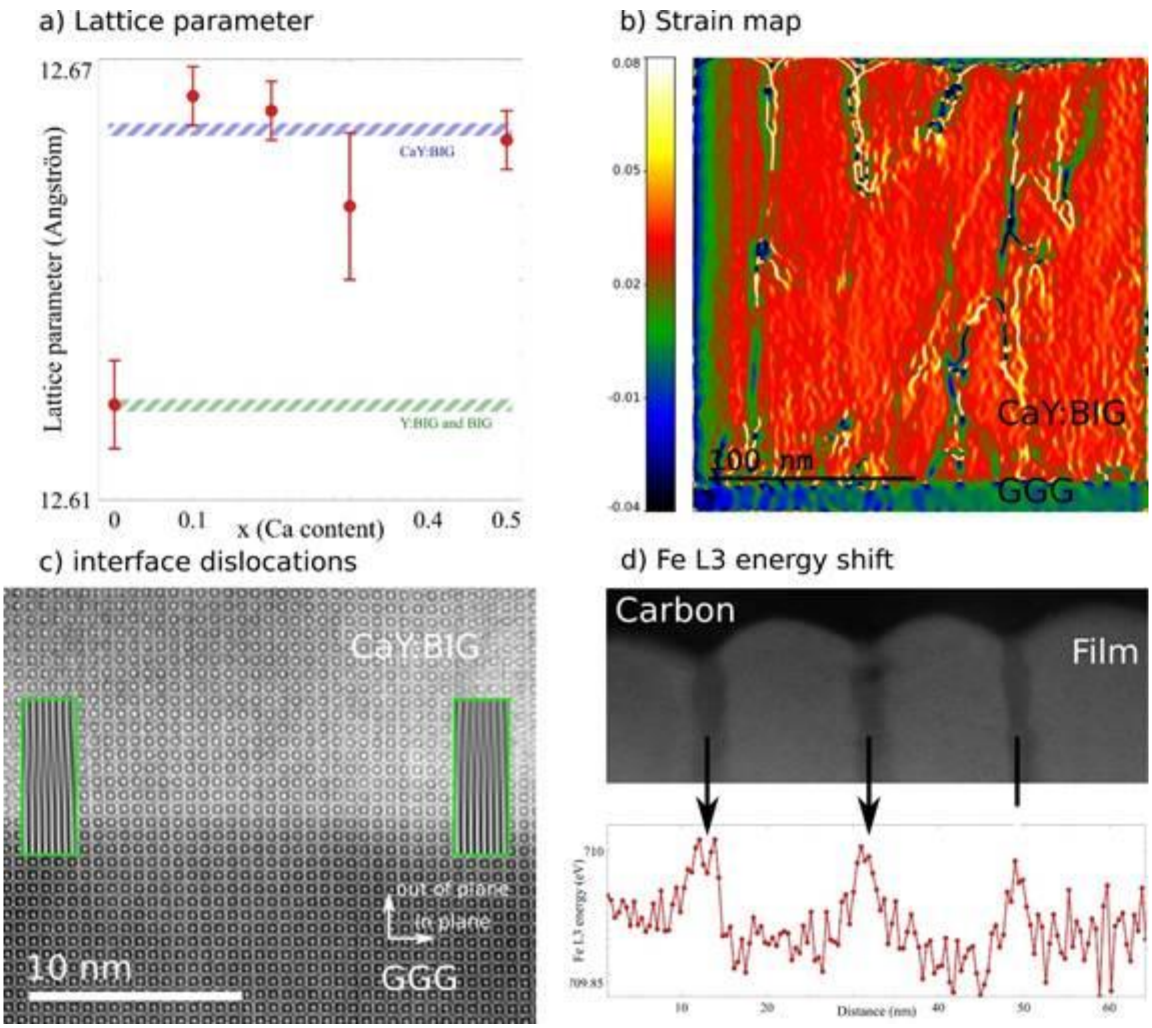

Fig. 1 a) Out of plane lattice parameter evolution as a function of Ca content. b) Out of plane strain map calculated by GPA. c) HAADF image at film/substrate interface with highlighted misfit dislocations. d) Fe L3 edge energy shift probed through several grains and defects at the top of the film.

X-ray diffraction experiments show that Ca increases the BIG unit cell volume (Fig1.a). Such a large unit cell is unusual for a garnet and the lattice mismatch between CaY:BIG and GGG is then around 2%.

Scanning transmission electron spectro-microscopy techniques (STEM/EELS) will enable us to have a better understanding of strain relaxation mechanisms and further relate them with the probed macroscopic physical properties.

Geometric phase analysis (Fig1.b) reveals a fast (over a few unit cells corresponding to 3 nm) and complete relaxed film (film/substrate lattice parameter ratio of 3%). Two strain relaxation mechanisms were observed, the formation of a secondary phase and misfit dislocations close to the film/substrate interface (Fig1.c). The respective role between the dislocations' density and the presence of impurities remains to be determined but dislocations seems to occur in the middle of the grain. On the other hand, the secondary phase is located mainly at the grain boundaries and have a much lower intensity contrast in HAADF image. For instance, these phases are Bi and Ca poor but Fe enriched as evidenced by EELS elemental mapping and correspond to an Y-doped iron oxide. A fine structure study of Fe L edge indicates an almost pure 3+ iron valence state in this Bi poor phase very much similar as the one of a pure hematite. The Fe L3 edge of neighbouring CaY:BIG grain is shifted to approximately 100 meV lower energy (Fig1.d) with respect to this secondary phase and show an overall fine structure still close to a Fe^{3+} with less marked crystal filed splitting. Such small energy shift are difficult to interpret since the BIG and secondary phase could have different local structure around the iron. Nevertheless, this energy shift might evidence that CaY:BIG have a small amount of divalent iron which tends to indicate the presence of oxygen vacancies. Such vacancies could explain the measured electrical transport properties. It is noteworthy that the observed very large unit cell of the CaY:BIG can favoured the formation of oxygen vacancies.

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